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Anion Modulated Structural Diversification in the Assembly of Cd(II) Complexes Based on a Balance-like Dipodal Ligand

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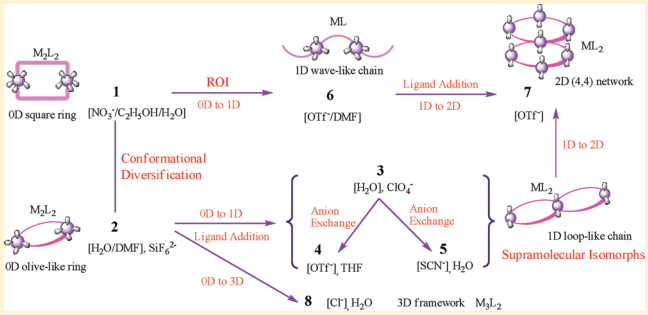
Supporting Information

ABSTRACT: Reaction of a balance-like dipodal ligand 2,6-bis(pyridiyl) hexahydro-4,8-ethenopyrrolo [3,4-f]isoindole-1,3,5,7-tetrone (3-pybtd) with various Cd(II) salts afforded eight complexes, namely, $[Cd_2(3\text{-pybtd})_2(NO_3)_4(C_2H_5OH)_2(H_2O)_2]$ (**1**), $[Cd_2(3\text{-pybtd})_2(SiF_6)_2(DMF)_4(H_2O)_2](H_2O)_4\cdot(DMF)_2$ (**2**), $\{[Cd(3\text{-pybtd})_2(H_2O)_4](ClO_4)_2\}_n$ (**3**), $\{[Cd(3\text{-pybtd})_2(OTf)_2]\cdot THF\}_n$ (**4**), $\{[Cd(3\text{-pybtd})_2(SCN)_2]\cdot(H_2O)_2\}_n$ (**5**), $[Cd(3\text{-pybtd})(OTs)_2(DMF)_2]_n$ (**6**), $[Cd(3\text{-pybtd})_2(OTs)_2]_n$ (**7**), and $\{[Cd_2(3\text{-pybtd})_2Cl_{10/3}][CdCl_{8/3}]\cdot(H_2O)_3\}_n$ (**8**). Complexes **1** and **2** are zero-dimensional (0D) square-like or olive-like dimeric M_2L_2 metallacycles, showing a pair of shape-modified molecular rectangles due to different conformations of the ligands and coordination orientation of the metal centers. Complexes **3**−**5** are one-dimensional (1D) looplike chains composed of olive-like M_2L_2 metallacycle building units as in **2**, showing 0D → 1D dimension increase via ligand addition, while complex **8** is a three-dimensional (3D) framework retaining the same olive-like M_2L_2 metallacycle, showing 0D → 3D dimension increase via linkage of μ_3-Cl bridged Cd(II) clusters. Complex **6** is a wave-like M_nL_n chain, possessing the same ML building units as in **1** but showing 0D → 1D dimension increase via ring-opening polymerization. Replacement of DMF molecules from the coordination sphere in **6** by the ligands resulted in a two-dimensional (2D) (4, 4) network of **7**, showing 1D → 2D dimension increase from **6** via ligand addition or 1D → 2D dimension increase from **3**−**5** via ring-opening polymerization. Complexes **3**−**5** also represent a series of supramolecular isomorphs displaying anion exchange properties. Electrospray ionization mass spectrometry (ESI-MS) studies in solution suggest that the discrete and infinite structures in **1**, **6**, and **7** are assembled from the same monomeric ML building blocks, which crystallize in a different way to lead to structural diversification via dimerization or polymerization during the crystallization.



INTRODUCTION

The design and synthesis of zero-, one-, two-, or three-dimensional (0D, 1D, 2D, or 3D) coordination assemblies by utilizing directional metal−ligand dative bonds has attracted considerable interest in recent years, which may bring both intriguing architectures and tailor-made applications in such fields as porosity, magnetics, optoelectronics, catalysis, and so on.[1,2] In particular, tremendous progress has been achieved in the modulated assembly of diversified coordination compounds from ingeniously designed ligand precursors with flexible and adjustable configurations and geometries.[3] The delicate balance between the adaptability of the organic ligands with the plentiful and versatile coordination modes of the central metals as well as the coparticipation of counteranions and solvent molecules leads to the formation of either discrete polynuclear complexes or infinite coordination polymers, affording great opportunities for the construction of novel and unusual metal−organic crystalline materials.[4,5]

Among which, dimension increase constitutes one important factor in the structural diversification of supramolecular structures. In general, the following cases might occur: (1) connection of low dimensional building units by the aid of various kinds of intermolecular weak interactions such as hydrogen bonds, $\pi-\pi$ interactions, metal−metal interactions, and metal-nonmetal interactions;[6] (2) alteration of the metal−ligand ratio as a result of reactant proportion, metal centers' coordination tendency or addition/subtraction of coordinated anions/solvent molecules;[7] (3) occurrence of "supramolecular isomerism",[8] and especially, ring-opening isomerization (ROI). Coordination compounds with either discrete or polymeric structures are observed in the ROI process, which are usually the products of thermodynamics or kinetics, respectively.[9,10]

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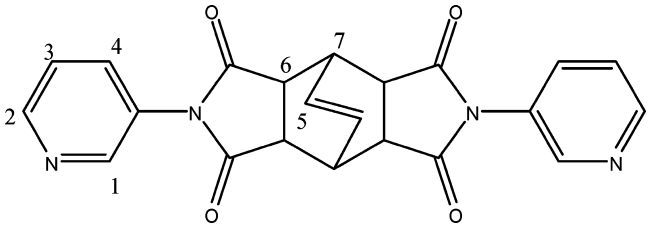
As a continuation of our previous work in fabricating 0D to 3D coordination complexes using ditopic ligands with an "arm−spacer−arm" type configuration[11] and further study of the mechanisms of the supramolecular isomerism, isomorphism, and structural transformation between the distinguishable structures, a balance-like dipodal ligand 2,6-bis(pyridiyl) hexahydro-4,8-ethenopyrrolo[3,4-*f*] isoindole-1,3,5,7-tetrone (3-pybtd) was prepared from a reaction of 3-aminopyridine with bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid dianhydride in acetic acid. The ligand contains a long central base with a bicyclo segment, resembling the bolster of a balance, while the two pyridyl coordinating rings may take alterable relative positions and conformations during the assembly, just like the two ends of a balance will swap their elevations subject to the weight change on each side. Herein we report eight complexes assembled from the reaction of 3-pybtd with different Cd(II) salts, in which the ligand takes three different kinds of conformations and affords crystal structures ranging from 0D molecular rings, 1D wave-like and loop-like chains, 2D (4, 4) nets to 3D coordination frameworks. Structural diversification with regard to dimension increase are observed in this series of Cd(II) compounds.

EXPERIMENTAL SECTION

All raw materials and solvents were obtained from commercial sources and used without further purification. Infrared spectra were measured on a Nicolet/Nexus-670 FT-IR spectrometer in the region 4000−400 cm^{-1} using KBr pellets. The powder X-ray diffraction (PXRD) was recorded on a Bruker D8 ADVANCE diffractometer. Thermogravimetric analysis (TGA) was performed in air and under 1 atm of pressure at a heating rate of 10 °C min^{-1} on a NETZSCH TG209 analyzer.

2,6-Bis(pyridiyl) hexahydro-4,8-ethenopyrrolo[3,4-f]-isoindole-1,3,5,7-tetrone (3-pybtd).



A mixture of bicycle (2,2,2) oct-7-ene-2,3,5,6-tetracarboxylic acid dianhydride (1.24 g, 5 mmol) and 3-amino-pyridine (0.9 g, 10 mmol) in acetic acid (10 mL) was heated to 120 °C with stirring for 4 h. On cooling, the off-white crude solid precipitated was filtered from the yellow solution, which was collected and washed several times with cold water. The thus obtained product was pure enough for synthesis of the complexes. Yield: 83.5%. Elemental analysis: Calc. for $C_{22}H_{16}N_4O_4$: C, 66.00; H, 4.03; N, 13.99; O, 15.98. Found: C, 65.85; H, 4.201; N, 13.89. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.632 (d, 2H, H2), 8.527 (s, 2H, H1), 7.582 (d, 2H, H4), 7.416 (q, 2H, H3), 6.406 (t, 2H, H5), 4.031 (s, 2H, H7), 3.299(s, 4H, H6), IR (KBr, cm^{-1}): 3465w, 1712s, 1484w, 1433m, 1384m, 1197m, 778w.

$[Cd_2(3\text{-pybtd})_2(NO_3)_4(C_2H_5OH)_2(H_2O)_2]$ (1). A solution of Cd-$(NO_3)_2$ (4.7 mg, 0.02 mmol) in C_2H_5OH (3 mL) was carefully layered over a solution of 3-pybtd (20 mg, 0.05 mmol) in CH_2Cl_2 (6 mL). The solution was left to stand for 1 week at room temperature, and colorless crystals appeared. IR(KBr, cm^{-1}): 3521s, 1713s, 1438m, 1299m, 808w, 779m. Elemental analysis: Calc. for $C_{48}H_{48}Cd_2N_{12}O_{24}$: C, 41.13; H, 3.45; N, 11.99. Found: C, 44.01; H, 3.547; N, 12.05.

$[Cd_2(3\text{-pybtd})_2(SiF_6)_2(DMF)_4(H_2O)_2](H_2O)_4\cdot(DMF)_2$ (2). A solution of $CdSiF_6$ (5.1 mg, 0.02 mmol) in THF (3 mL) was carefully mixed with a solution of 3-pybtd (8 mg, 0.02 mmol) in DMF (3 mL). The clear filtrate was left in a test tube, and slow diffusion of Et_2O into the filtrate resulted in precipitation of colorless crystals. IR(KBr, cm^{-1}): 3480m, 1714s, 1660s, 1486m, 1436m, 1384s, 1204m, 1188m, 781m, 746m, 701m, 483w. Elemental analysis: Calc. for $C_{62}H_{86}Cd_2F_{12}N_{14}O_{20}Si_2$: C,40.11; H, 4.64; N,10.57; Found: C, 39.73; H, 4.44; N,10.21.

$\{[Cd(3\text{-pybtd})_2(H_2O)_2]\ (ClO_4)_2\cdot(H_2O)_2\}_n$ (3). A solution of Cd-$(ClO_4)_2$ (6.2 mg, 0.02 mmol) in C_2H_5OH (3 mL) was carefully layered over a solution of 3-pybtd (20 mg, 0.05 mmol) in CH_2Cl_2 (6 mL). The solution was left to stand for 1 week at room temperature, and colorless crystals appeared. IR (KBr, cm^{-1}): 3369w, 3055m, 1778m, 1700s, 1487s, 1436s, 1379s, 1200s, 1181s, 1101s, 1050s, 773m, 731m, 702m, 621m. Elemental analysis: Calc. for $C_{44}H_{40}CdCl_2N_8O_{20}$: C, 44.63; H, 3.40; N, 9.46; Found: C, 44.58; H, 3.315; N, 9.41.

$\{[Cd(3\text{-pybtd})_2(OTf)_2]\cdot(THF)_2\}_n$ (4). A solution of $Cd(OTf)_2$ (8.2 mg, 0.02 mmol) in THF (3 mL) was carefully mixed with a solution of 3-pybtd (8 mg, 0.02 mmol) in DMF (3 mL). The clear filtrate was left in a test tube, and slow diffusion of Et_2O into the filtrate resulted in precipitation of colorless crystals after 4−5 days. IR(KBr, cm^{-1}): 3465w, 2931w, 1770m, 1710s, 1581m, 1484s, 1430s, 1380s, 1193s, 777s. Elemental analysis: Calc. for $C_{52}H_{47}CdF_6N_8O_{17}S_2$ ($\{[Cd(3\text{-pybtd})_2(OTf)_2]\cdot(THF)_{1.5}\cdot(H_2O)_{1.5}\}_n$): C, 46.38; H, 3.52; N, 8.32; Found: C, 46.37; H, 3.345; N, 8.23.

$\{[Cd(3\text{-pybtd})_2(SCN)_2]\cdot(H_2O)_2\}_n$ (5). A buffer layer of a solution of ethanol (1 mL) was carefully layered over a solution of 3-pybtd (8 mg, 0.02 mmol) in CH_2Cl_2 (6 mL). Then a solution of $Cd(OTf)_2\cdot 6H_2O$ (8.2 mg, 0.02 mmol) and NaSCN (0.8 mg, 0.01 mmol) in ethanol (3 mL) was layered over the buffer layer. The solution was left to stand for 1 week at room temperature, and colorless crystals appeared. IR(KBr, cm^{-1}): 3434m, 2068s, 1716s, 1484m, 1436s, 1375s, 1174m, 720w. Elemental Analysis: Calc. for $C_{47}H_{36}CdCl_{2/3}N_{10}O_9S_2$ ($\{[Cd(3\text{-pybtd})_2(SCN)_2]\cdot(H_2O)_{2/3}\cdot(CH_2Cl_2)_{1/3}\cdot(C_2H_5OH)_{1/3}\}_n$): C, 52.03; H, 3.34; N, 12.91; Found: C, 51.67; H, 3.361; N, 12.91.

$[Cd(3\text{-pybtd})(OTs)_2(DMF)_2]_n$ (6). A solution of $Cd(OTs)_2$ (9 mg, 0.02 mmol) in THF (3 mL) was carefully mixed with a solution of 3-pybtd (8 mg, 0.02 mmol) in DMF (3 mL). The clear filtrate was left in a test tube, and slow diffusion of Et_2O into the filtrate resulted in precipitation of colorless crystals after 4−5 days. IR(KBr, cm^{-1}): 2429w, 1718s, 1647s, 1488w, 1437m, 1382m, 1239m, 1184s, 1170s, 1121m, 1035m, 1009w, 783w, 679s, 567m. Elemental analysis: Calc. for $C_{42}H_{44}CdN_6O_{12}S_2$: C, 50.38; H, 4.43; N, 8.39; Found: C,50.53; H, 4.283; N, 8.20.

$[Cd(3\text{-pybtd})_2(OTs)_2]_n$ (7). A buffer layer of a solution of ethanol (1 mL) was carefully layered over a solution of 3-pybtd (8 mg, 0.02 mmol) in CH_2Cl_2 (6 mL). Then a solution of $Cd(OTs)_2$ (9 mg, 0.02 mmol) in ethanol (3 mL) was layered over the buffer layer. The solution was left to stand for 1 week at room temperature, and colorless crystals appeared. IR (KBr, cm^{-1}): 3467w, 3079w, 1781m, 1719s, 1582m, 1489s, 1437s, 1380s, 1253 m, 1239s, 1202s, 1184s, 1121s, 1034m, 1012m, 781s, 731m, 700s, 568m.

$\{[Cd_2(3\text{-pybtd})_2Cl_{10/3}][CdCl_{8/3}]\cdot(H_2O)_3\}_n$ (8). A buffer layer of a solution of ethanol (1 mL) was carefully layered over a solution of 3-pybtd (8 mg, 0.02 mmol) in CH_2Cl_2 (6 mL). Then a solution of $CdCl_2$ (3.7 mg, 0.02 mmol) and NaSCN (0.8 mg, 0.01 mmol) in ethanol (3 mL) was layered over the buffer layer. The solution was left to stand for 1 week at room temperature, and colorless crystals appeared. IR(KBr, cm^{-1}): 3482w, 3081w, 2923w, 2067w, 1715s, 1489m, 1438m, 1365m, 1207m, 1173m, 785m, 701m. Elemental Analysis: Calc. for $C_{44}H_{38}Cd_3Cl_6N_8O_{11}$: C, 37.62; H, 2.73; N, 7.98; Found: C, 37.90; H, 2.621; N, 7.88.

X-ray Crystallography. Single-crystal X-ray diffraction measurements were carried out on Agilent Gemini S Ultra CCD diffractometer at 150 K with graphite monochromated Mo−K_α radiation (λ = 0.7107 Å) for complexes **1**, **3**, and **5**−**7**, with Cu−K_α radiation (λ = 1.54178 Å) for complexes **2**, **4**, and on Rigaku IP diffractometer at 150 K with graphite monochromated Mo−K_α radiation (λ = 0.7107 Å) for complex **8**. The structures were solved by direct methods and refined using the full-matrix least-squares method against F^2 using SHELXL software.[12] The coordinates of the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. In complexes **3** and **8**, the guest molecules are

Table 1. Crystal Data and Structure Refinement Summary for Complexes 1−8

complex	1	2	3	4
formula	$Cd_2C_{48}H_{48}N_{12}O_{24}$	$Cd_2C_{62}H_{86}F_{12}N_{14}O_{20}Si_2$	$CdC_{44}H_{36}Cl_2N_8O_{20}$	$CdC_{54}H_{48}F_6N_8O_{16}S_2$
formula weight	1401.78	1856.43	1180.11	1355.55
crystal system	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.3783(17)	12.7105(2)	8.9845(3)	9.597(5)
b (Å)	13.0129(19)	15.6823(2)	12.5760(6)	11.831(5)
c (Å)	14.9959(18)	19.4729(3)	14.3161(6)	13.041(5)
α (°)	107.940(12)	90	67.106(4)	102.587(5)
β (°)	103.901(15)	101.276(2)	80.345(3)	95.215(5)
γ (°)	93.989(15)	90	71.350(4)	107.603(5)
V (Å^3)	1313.5(4)	3806	1410.15(10)	1357.7(10)
Z	1	2	1	1
D_{calc} (g cm^{-3})	1.772	1.620	1.390	1.658
μ (mm^{-1})	0.910	5.729	0.558	0.580
goodness-of-fit on F^2	1.067	1.030	1.031	1.004
R_1 [$I > 2\sigma(I)$], wR_2 (all data)	0.0360, 0.0968	0.0364, 0.0989	0.0761, 0.2453	0.0460, 0.1250
complex	5	6	7	8
formula	$C_{46}H_{36}CdN_{10}O_{10}S_2$	$C_{42}H_{44}CdN_6O_{12}S_2$	$C_{58}H_{46}CdN_8O_{14}S_2$	$Cd_3C_{44}H_{32}Cl_6N_8O_{11}$
formula weight	1065.40	1001.35	1255.55	1398.71
crystal system	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$C2/c$
a (Å)	6.8091(4)	18.0816(10)	9.7329(5)	25.5812(6)
b (Å)	10.9815(7)	9.8335(5)	12.0003(6)	13.7824(3)
c (Å)	15.5769(10)	25.7919(6)	25.0949(13)	13.6089(4)
α (°)	98.267(5)	90	77.713(4)	90
β (°)	102.055(5)	105.674(5)	83.216(4)	97.7670(10)
γ (°)	96.478(5)	90	72.719(4)	90
V (Å^3)	1114.88(12)	4415.4(3)	2729.9(2)	4754.1(2)
Z	1	4	2	4
D_{calc} (g cm^{-3})	1.587	1.506	1.528	1.954
μ (mm^{-1})	5.415	0.658	0.553	1.737
goodness-of-fit on F^2	1.026	1.008	1.009	1.033
R_1 [$I > 2\sigma(I)$], wR_2 (all data)	0.0303, 0.0794	0.0519, 0.1561	0.0566, 0.1137	0.0258, 0.1284

disordered severely, it is too hard to refine them. According to the elemental analysis result, we just refined the first two high density Q peaks to oxygen atoms, corresponding to two water molecules (site occupancy is 1 while Cd is 0.5), and they cannot add hydrogen atoms appropriately, so we let the oxygen atoms stay isolated. One coordinated DMF molecule in complex **6** is disordered so it was treated as two parts. Crystallographic data and other pertinent information for **1**−**8** are summarized in Table 1. Selected bond lengths and bond angles are listed in Table S1. CCDC numbers for complexes **1**−**8** are 862380−862387.

RESULTS AND DISCUSSION

I. Crystal Structures. *0D Molecular Rings in Complexes **1**−**2**.* Single crystal X-ray analysis reveals that complex **1** crystallizes in the triclinic system with a space group $P\bar{1}$. As shown in Figure 1a, the overall coordination geometry of the Cd(II) ion can be described as a distorted pentagonal bipyramid consisting of two N(Py) donors from two different ligands on the apical positions, and the horizontal planes are occupied by three O atoms from two different NO_3^- anions (affording two and one O atoms, respectively) as well as two O atoms from H_2O and C_2H_5OH molecules. Two 3-pybtd ligands take the "*cis*-U" conformation (Scheme 1) like pincers to link two Cd(II) ions into a 0D square-like molecular ring ($d_{Cd\cdots Cd}$ = 10.6 Å), and the two N−Cd bonds from two different 3-pybtd ligands are almost linear (∠N1CdN4 = 172.12°). Adjacent molecular rings are further packed together by $\pi\cdots\pi$ interactions between neighboring Py rings (d = 3.528 Å) and C−H···O hydrogen bonds between 3-pybtd and the coordinating NO_3^- anions (d = 2.959 Å).

Complex **2** crystallizes in the monoclinic system with the space group $P2_1/n$. As shown in Figure 2, the Cd(II) center is six-coordinated, exhibiting a CdN_2O_2OF environment composed of two N atoms from two independent 3-pybtd ligands, one O atom from H_2O molecule, two O atoms from DMF, and one fluorine atom from hexafluorosilicate anion. Different from the coordination environment in complex **1**, the two N−Cd bonds from two 3-pybtd ligands are almost perpendicular (∠N1CdN4 = 85.61°), and therefore, each 3-pybtd takes on the "*cis*-L" conformation (Scheme 1). The participation of H_2O, DMF molecules and hexafluorosilicate anion helps to satisfy the coordination sphere and a 0D olive-like M_2L_2 molecular ring is obtained (Cd···Cd distance is about 15.0 Å), whose shape is quite different from the square-like ring in complex **1**. The molecular rings are connected together through C−H···F (d = 2.351−2.534 Å) and O−H···F (d = 1.893−2.064 Å) hydrogen bonds from SiF_6^{2-} anions to the C−H groups on the ligand and coordinated H_2O. Solvated H_2O molecules also form abundant hydrogen bonds with the coordinated SiF_6^{2-} anions (d = 2.812 Å) and C−H groups on the ligand (d = 2.684 Å).

*II. 1D Chain Structures and Supramolecular Interactions in Complexes **3**−**6**.* The common structural feature in

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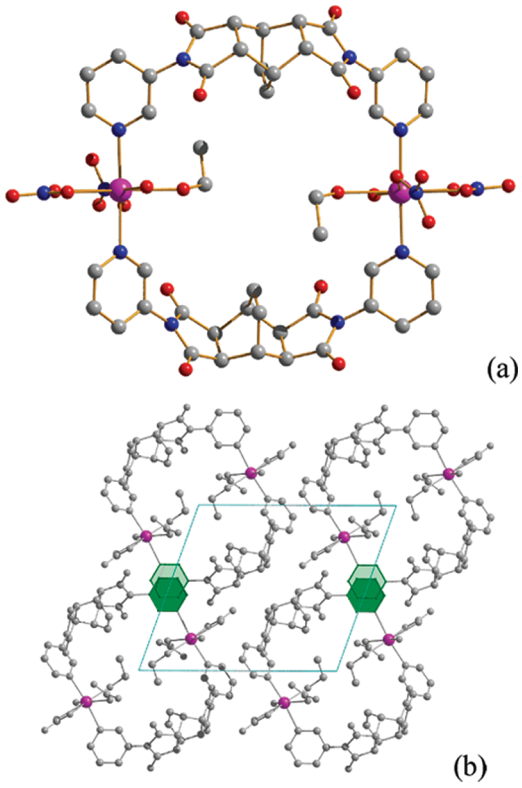


Figure 1. (a) 0D molecular ring in complex **1**. (b) $\pi\cdots\pi$ interactions between neighboring rings.

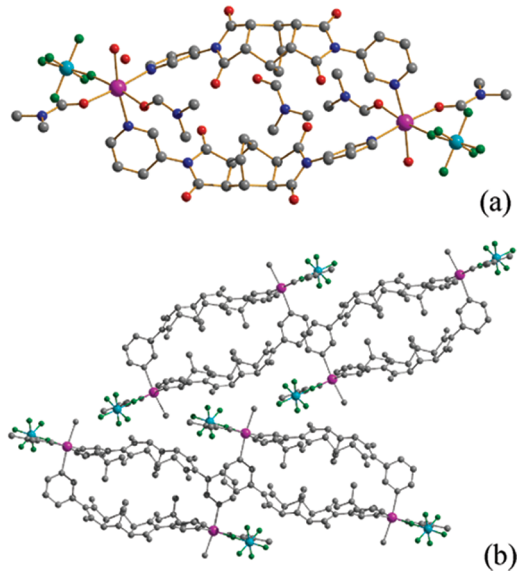
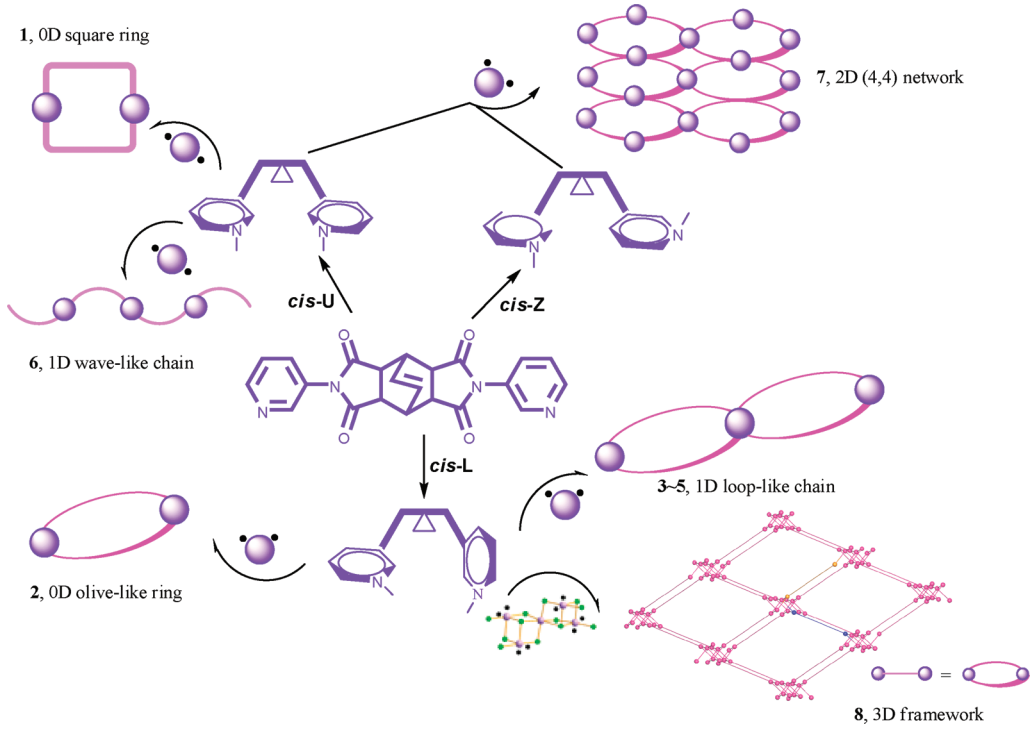


Figure 2. (a) 0D molecular ring in complex **2**. (b) Crystal packing of the 0D rings, guest molecules are omitted for clarity.

complexes **3**−**5** is that 3-pybtd takes on the "*cis*-L" conformation and the compound crystallizes in triclinic $P\bar{1}$ space group. In complex **3**, the Cd(II) ions are in an octahedral coordination geometry in which four N atoms from four different 3-pybtd ligands compose the horizontal plane and two O atoms from H_2O molecules occupy the apexes. The four N−Cd bonds around each Cd(II) ion are coplanar and fall in an orthogonal position (∠NCdN = 85.7 and 94.3°). Different from the discrete structure in complex **2**, where DMF molecules hold up two positions around each Cd(II), the solvent CH_2Cl_2 does not participate in coordination in complex **3**. Therefore, while preserving the M_2L_2 repeating rings similar to **2**, double amounts of 3-pybtd ligands are coordinated with Cd(II) centers into an infinite looplike 1D chain. The Cd···Cd

Scheme 1. Conformation Modes of 3-pybtd, Coordination Orientations of Blocked Cd(II) Metal Centers and Formation of Different Coordination Assemblies



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distance within the M_2L_2 basic ring is 15.6 Å, similar to that in complex **2**. No guest molecule is hosted inside the basic M_2L_2 ring, which may be due to the olive-like shape of the M_2L_2 ring. Instead, waving channels are present between adjacent looplike chains, in which uncoordinated ClO_4^- anions and water molecules are enclosed and interact with the chains through C−H···O hydrogen-bonding interactions (Figure 3b).

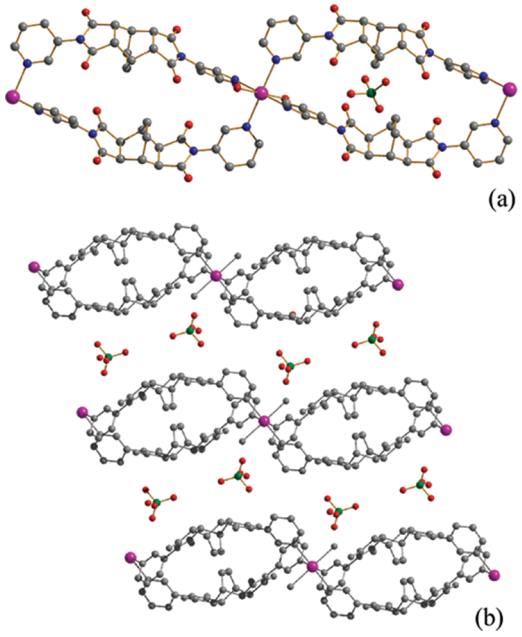

Figure 3. (a) 1D looplike chain in complex **3**. (b) Guest-filled crystal packing of the 1D chains, showing inclusion of ClO_4^- anions and water molecules outside the M_2L_2 basic rings.

The coordination environment and crystal packing in complexes **4**−**5** are similar to those in complex **3**, except that two $CF_3SO_3^-$ or SCN^- anions instead of H_2O molecules help to satisfy the octahedral coordination geometry and form 1D looplike chain. THF or H_2O solvent molecules are filled between the chains. Complexes **3**−**5** constitute a series of supramolecular isomorphs.

By contrast, complex **6** exhibits a polymeric 1D wave-like chain structure and crystallizes in C2/c space group. Each Cd(II) ion has an octahedral coordination geometry with four O atoms from two OTs^- anions and two DMF molecules positioned on the basal plane and two N atoms from two 3-pybtd ligands on the apexes. The 3-pybtd ligand takes the *cis*-U conformation similar to that in complex **1**, but in comparison to the M_2L_2 metallacycle in **1**, the 3-pybtd ligands in complex **6** join the Cd(II) ions in a head-to-tail fashion to form an infinite 1D wave-like chain. Viewed along the *b* direction, the 1D wave-like chains are interlaced into a 2D plane (Figure 4b).

III. 2D (4, 4) Networks in Complex ***7****.* In complex **7**, 3-pybtd ligands have two different kinds of conformations, *cis*-U and *cis*-Z (Scheme 1). Each Cd(II) center is coordinated with four N atoms from four ligands, as well as two O atoms from OTs^- anions, satisfying an octahedral coordination geometry, as shown in Figure 5a. The four N−Cd bonds around each Cd(II) ion are almost coplanar (∠NCdN = 85.6 and 94.4°). Because of the different conformations adopted by the ligands, dumbbell-like and olive-like M_4L_4 connected patterns are coexisted in the lattice (Figure 5b). The network can also be represented by (4, 4) topological grids when using metal centers as connecting

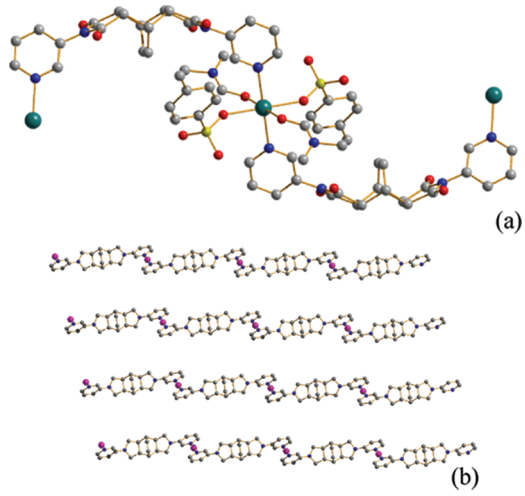

Figure 4. (a) The coordination unit in complex **6**. (b) Crystal packing of the 1D chains along the *b* direction, the coordinated anions and DMF molecules are omitted for clarity.

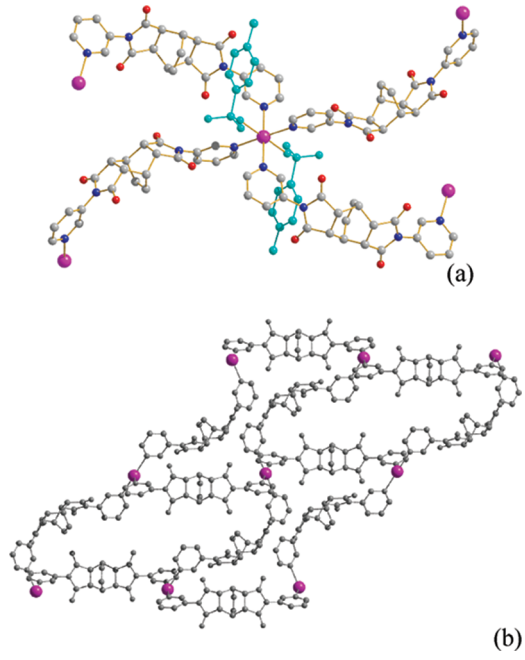

Figure 5. The crystal structures of complex **7**, (a) coordination environment of Cd(II) ion, (b) the dumbell-like and olive-like M_4L_4 connection patterns (coordinated OTs^- anions are omitted for clarity).

nodes. The M_4L_4 rhombic grid has an average size of 15.0 × 12.7 Å, but the extending Ph rings on the OTs^- anions possess most of the spaces in the cavity.

IV. 3D Frameworks Sustained by Cd String in Complex ***8****.* In complex **8**, there are two different kinds of metal centers, in which Cd1 is coordinated by two 3-pybtd ligands as well as four bridging Cl^- anions, while Cd2 is connected only by six Cl^- anions (Figure 6a). Intriguingly, the 3D structure of **8** contains infinite cadmium strings formed through Cd−Cl−Cd bonds, which consist of Cl^- anions adopting a μ- or μ_3-bridging mode to link the two kinds of Cd(II) centers into a string (Figure 6b). This kind of linkage is very special which relates to the $Cd_4(Cl)_2(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)_2$ core structure reported by Wei et al,[13] in which four cadmium atoms in two different kinds of

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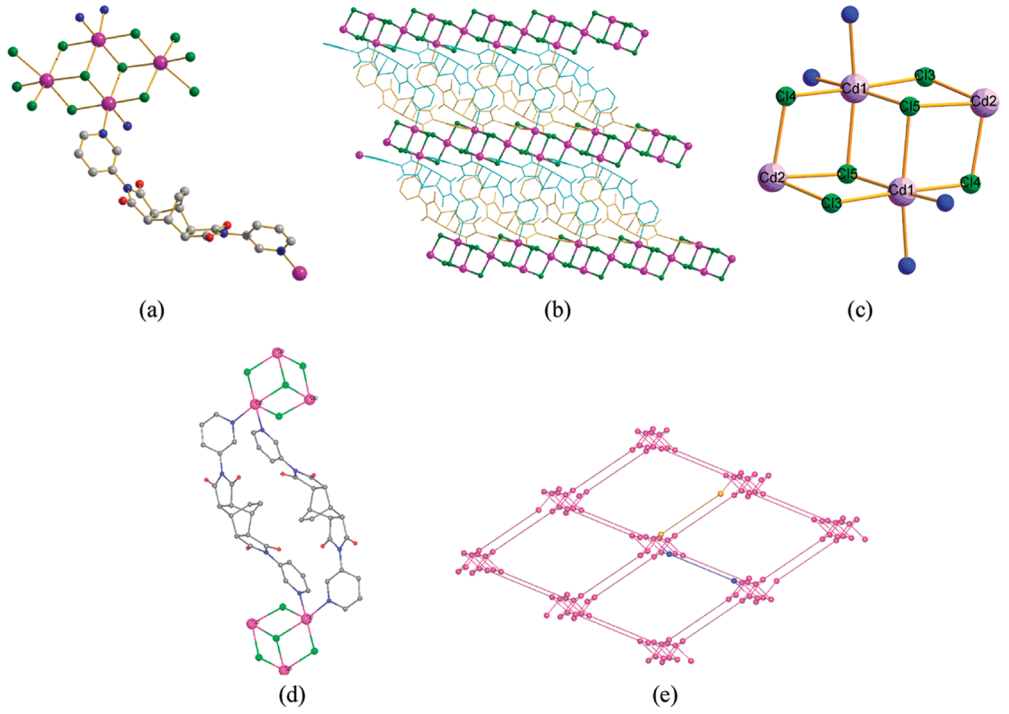
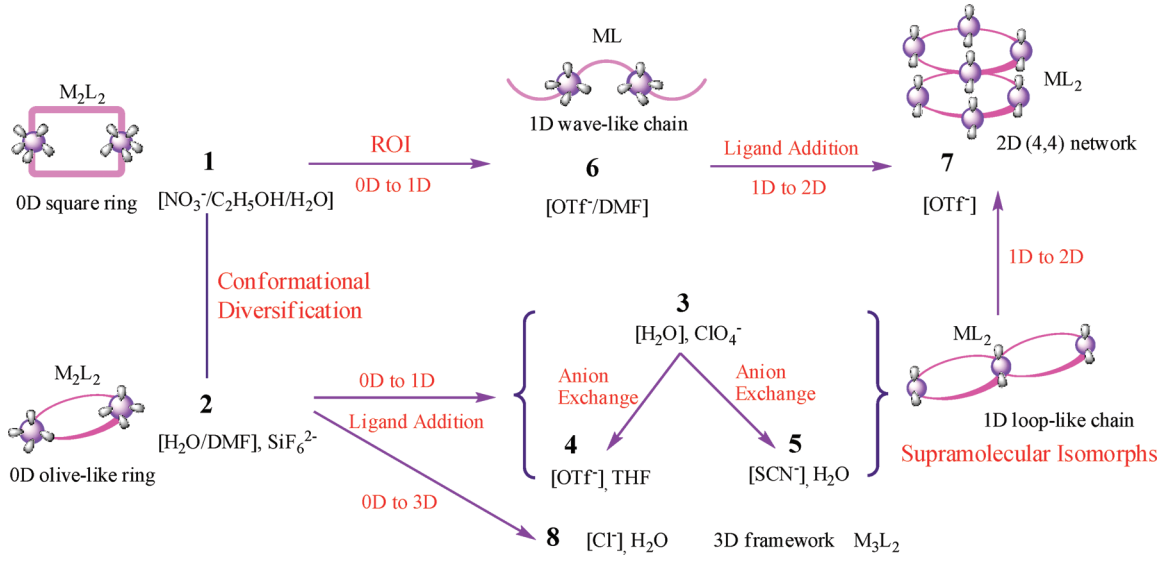


Figure 6. The crystal structures of complex **8**, (a) coordination environment of Cd(II) ions, (b) crystal packing view along the *b* direction showing the cadmium string formed by μ- and μ_3-Cl bridging, (c) the structure of Cd(II) cluster linked by Cl atoms, (d) the M_2L_2 olive-like ring, (e) 3D topological mode (the loop formed between two Cd1 by two ligands is abbreviated to be a line, the atoms and lines in orange and blue are the same with the purple ones to clearly show their non-coplanar positions).

Scheme 2. The Structure Relationship among Different Cd(II) Complexes



coordination environment arrange as a prism by the linkage of μ- and μ_3-Cl atoms. In comparison, herein, the two different kinds of Cd(II) centers arrange in a double-stranded strings along the *b* direction, in which two μ-Cl, two μ_3-Cl, two Cd1 and one Cd2 atoms form a box-like formation but shorting of one corner (Figure 6c). The mean Cd-μ-Cl bond distance (2.590 Å) is shorter than the mean Cd-μ_3-Cl bond distance (2.897 Å). The shortest Cd1−Cd1 separation is 3.935 Å and Cd1−Cd2 separation is 4.014 Å. In complex **8**, 3-pybtd ligands take the *cis*-L configuration. As shown in Figure 6d, two Cd1 centers are connected by two ligands into an olive-like ring similar to those in **2**−**5**. If we simplify the linkage between the two Cd1 centers to a line, a 3D framework can be represented in complex **8** (Figure 6e). The solvated water molecules form O−H···O hydrogen bonds with the acetyl O atoms on the ligand ($d_{O1\cdots O2w}$ = 2.673 Å, $d_{O2\cdots O2w}$ = 2.765 Å).

Conformation Modes of 3-pybtd. The ligand 3-pybtd incorporates a bicyclo central base and two Py ending groups which can take variable coordination orientations. In our previous work with similar ligand 2,6-bis(pyridin-3-ylmethyl)-hexahydro-4,8-ethenopyrrolo[3,4-*f*]isoindole-1,3,5,7-tetrone,[10b] the free rotatable $-CH_2$ group makes the two Py ends in the ligand able to take either *cis*- or *trans*-position relative to the central bicyclo ring when coordinated with different metal ions.

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Comparatively, in this series of complexes assembled from 3-pybtd without the linkage of $-CH_2$, the bicyclo ring and two Py ends should always take the *cis*- positions, but the free rotating of the C−N bond still affords different kinds of coordination orientations on the two terminal Py rings. The two ends swap from almost parallel to perpendicular, and then antiparallel, which are assigned as *cis*-U (**1**, **6**, 7), *cis*-L (**2**−**5**, **8**), and *cis*-Z (**7**) conformations respectively, as depicted in Scheme 1.

Coordination Orientation of Blocked Cd(II) Metal Centers. Originally, the Cd(II) center has an octahedral coordination sphere with O_h symmetry. But in complexes **1**−**8**, some coordination positions are blocked by coordinated anions or solvent molecules. Therefore, different kinds of coordination orientations are left for the ligands, and diverse structures resulted in the final structures. In complexes **1** and **6**, after occupation of the anions (NO_3^- or OTs^-) and solvents (H_2O/C_2H_5OH or DMF), two apical vertices with linear orientations are left for the ligands to coordinate with. As a consequence, normal square ring or wave-like chain is obtained. In complexes **2** and **8**, after the blockage of H_2O/DMF molecules and hexafluorosilicate anion or Cl−Cd cluster, two coordination ends with right-angle positions are left for the ligands on each Cd(II) center. Therefore, the M_2L_2 ring in **2** or the similar units in **8** are more flat and olive-like. While in complexes **3**−**5** and **7**, anions or solvent molecules with lower coordination abilities such as ClO_4^-, THF, or CH_2Cl_2 cannot help to terminate the coordination of Cd(II) into discrete structures. Therefore, four ligands coordinate with each Cd(II) center in a right crossed coplanar way, and the M_2L_2 ring units in these complexes are also olive-like. To adapt to the blocked metal centers with different coordination orientations stated above, the ligands also take varied conformations. In general, the *cis*-U conformation is more suited with the metal center with linear coordination orientation, while *cis*-L and *cis*-Z conformations are more adaptable with right angular orientations.

Structural Diversification among the Complexes. As a summary, the structural relationship among the eight complexes are shown in Scheme 2. We can see that the structural diversification can be classified into the following types:

(i) Conformational diversification resulted from different conformation of the ligands and coordination units. As stated above, subject to the changes in the blocked Cd(II)'s coordination orientations by the participation of various anions and solvents, the 3-pybtd ligands take either *cis*-U or *cis*-L configuration in complexes **1** and **2**. Although they both have the M_2L_2 formula, distinct 0D square or olive-like ring structures are formed. Therefore, conformational diversification is derived.[4,14]

(ii) Ring-opening isomerization (ROI).[7−9] In complexes **1** and **6**, the ligands both take the *cis*-U configuration and the metal centers all serve as 2-conneting nodes. However, **1** has 0D square discrete structures and **6** shows up as 1D wave-like infinite chain. Formation of **6** may be visualized as through a ring-opening isomerization process from **1**; namely, the M_2L_2 square opens the ring to polymerize. ESI-MS in CH_3CN solution proves that they both have the basic monomeric $[ML]^{2+}$ or $[ML{\cdot}OTs]^+$ species. This shows that both complexes **1** and **6** are originated from the similar ML monomers in solution, although different crystallization processes result in disparate structures. As generally believed, the cyclic structures are usually thermodynamically preferred, while the polymeric chains are more kinetically favored.[9e] Since the energy difference between the two structures is quite small, they can be easily affected by various external influences such as the introduction of different anions and solvents.[10,15] Similarly, in 1D looplike chain of **4** and 2D (4,4) net of **7**, the participated anions are both OTf^- and the metal/ligand ratio are both 1:2. The two complexes can be viewed as a pair of ROI isomers. During the ring-opening process of **4** into **7**, half of the ligands change their conformation slightly from *cis*-L to *cis*-Z to better adapt to the higher dimensional network structure.

(iii) Supramolecular isomorphs. In complexes **3**−**5**, although the coordination anions or solvent molecules are different, they represent a similar looplike-chain structure. Anion exchange study shows that the immersion of **3** in NaSCN solution results in the disappearance of the IR vibration bands of ClO_4^- (~1050−1100 cm^{-1}), and the appearance of the band for SCN^- anions (~2068 cm^{-1}) (Figure S1). The immersion of **3** in $Cd(CF_3SO_3)_2$ solution also results in the obvious diminishing of the IR vibration bands of ClO_4^- (Figure S2). This shows that the water molecules in the coordination sphere can be replaced by SCN^- or $CF_3SO_3^-$ anions, but reverse transitions cannot happen.

(iv) Ligand addition or cluster induced dimension increase. The removal of anions or solvent molecules from the coordination sites of Cd(II) center will lead to ligand addition and dimension increase as observed in complexes **1**−**8**. In complexes **1**, **2**, and **6**, five or four coordination sites of the metal center are blocked by coordinated anions or solvent molecules. The ligands only have two sites left. Therefore, both the ligands and metals are 2-connected, and their molar ratio in the final structure is 1:1. Low dimensional 0D molecular ring or 1D chains are formed in the three complexes. Otherwise, if only two coordination sites of the Cd(II) centers are blocked by anions or solvent molecules, each Cd(II) connects four ligands while each ligands connects two metals. Their ratio changes to 1:2. That is, more ligands are applied to satisfy the coordination sphere and this will link the compounds into higher dimensions. As a result, the 1D $\{ML\}_n$ chain in **6** turns into 2D $\{ML_2\}_n$ type (4,4) net in complex **7**, for which the dimensionality increases from 1D to 2D. Similarly, the M_2L_2 0D olive-like ring of **2** turns into ML_2 type 1D looplike chain in complexes **3**−**5**, showing a 0D → 1D dimension increase due to ligand addition. On the other hand, the introduction of Cd(II) cluster centers connected by μ-Cl bridges in complex **8** with multiple coordination sites results in 1D → 3D dimension increase. Although there still remains similar M_2L_2 olive-like ring building units as in complexes **2**−**5**, the metal−ligand ratio is increased to 3:2. ESI-MS studies of complexes **6** and **7** in CH_3CN solution shows that both complexes have similar fragment species such as $[Cd{\cdot}L{\cdot}OTs{\cdot}2(CH_3CN)]^+$ (766), $[Cd{\cdot}L{\cdot}OTs{\cdot}2(CH_3CN){\cdot}CH_3OH]^+$ (798), $[Cd{\cdot}L_2{\cdot}OTs{\cdot}CH_3CN]^+$ (1126) (Figure S3). This proves the intrinsic relationship between the two structures.

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CONCLUSIONS

In summary, eight Cd(II) complexes have been assembled from a balance-like dipodal ligand 2,6-bis(pyridiyl) hexahydro-4,8-ethenopyrrolo[3,4-f]isoindole-1,3,5,7-tetrone (3-pybtd) and different Cd(II) salts. The complexes display structural diversification with structures ranging from 0D to 3D, which was modulated by different anions and correlated through a dimension increase pathway. Complexes **1** and **6** show an ROI relationship while complexes **1** and **2** display conformational diversification. These compounds have the same metal−ligand ratio of 1:1, showing up as 0D metallacycle ring or 1D wave-like chain. When fewer anions or solvent molecules while double the amount of ligands are coordinated with Cd(II) centers, 1D looplike chain (**3**−**5**) or 2D (4, 4) network (**7**) is obtained, resulting in a metal−ligand ratio of 1:2. Furthermore, the application of μ-Cl bridged Cd(II) clusters affords a 3D framework structure in complex **8**, with a metal−ligand ratio of 3:2. Solution study also proves the intrinsic relationship along the assembly process and structural diversification of the complexes.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data (CIF format), IR spectra, PXRD patterns, and ESI-MS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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